

ПРОБЛЕМЫ ГЕОЛОГИИ И ОСВОЕНИЯ НЕДР

CHARACTERIZATION OF ORGANIC MATTER IN THE ROCKS OF THE DMITRIEVSKOE OIL SHALE DEPOSIT USING ROCK-EVAL PYROLYSIS

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The issue of research of organic matter in rocks takes an important place in organic geochemistry. According to the organic theory of petroleum origin the rocks enriched organic matter and achieved a necessary maturity could generate oil and gas in geological past. Oil shales are one of such rock types.

The Rock-Eval pyrolysis method, proved itself and widely used, enables the researcher to evaluate the maturity degree, quality and quantity of organic matter in a rock. In the process of this method pyrolysis of the organic matter in rocks is realized with programmed heating in an inert atmosphere with the detection of degradation products of organic matter [2]. Parameter characterizing the maturity of organic matter is temperature T_{max} .

The quality of organic matter is characterized by the hydrogen (HI) and oxygen (OI) indices parameters, and its quantity is characterized by the content of total organic carbon (TOC). In turn, the fraction of mineral carbon is characterized by the MINC parameter.

Objects of study are rock samples from the Dmitrievskoe deposit. Administratively, it is located near the village of Dmitrievka, Barzas district, Berezovsky town, Kemerovo region. Geographically, the deposit belongs to the right bank of the Barzass River, between its tributaries Pereboy and Topka.

The deposit is an oil shale formation that comes out to the surface. It can be traced at a distance of about 5 km from the village of Odinochniy in the north to the village of Dmitrievka in the south and monoclinally falls to the southwest at an angle of 20–25 °.

According to [1], the shale formation is a package of layers with a total thickness of 35 to 55 m. From the south to the north, the total thickness gradually decreases, but the thickness of organic carbon-poor rock layers lying between individual layers of oil shales increases. Maximum thickness (up to 55 m) has found out in the middle part of the deposit namely about 1,5–2,0 km from the village of Dmitrievka. To the south-east, on the Chernushka river, the thickness of the oil shale deposit decreases to 38 m, and to the north-west, on the Trudnoy river, it decreases to 40 m.

The Dmitrievskoe deposit rocks are carbonated from homogeneous to fissile from gray-brown to dark-brown marls. They have single inclusions and fine dispersion of carbonized plant detritus, single remains of psilophytes stems. Carbonatization is presented as an incrustation of brownish-white and grayish-white calcite. Fibres of bitumen. Conchoidal fracture.

The oil shale layers belong to the Dmitrievka-Pereboy formation, which has a rather uncertain stratigraphic position. It is underlied by the Early-Middle Devonian sediments of the Krasnogorsk formation and is transgressively overlid by sediments of the Upper Devonian. According to the results of research Gutak Ya.M. [1] relates the formation to the Middle Devonian.

Based on the data obtained from the pyrolysis results the geological and geochemical section of the Dmitrievskoe deposit has constructed (Fig.). Different organic carbon content has allowed to divide Dmitrievka-Pereboy formation into five layers: 0,3–1,5 % – layer I; 4,0–7,8 % – layer II; 3,5–6,0 % – layer III; 6,0–8,1 % – layer IV; 0,5–4,3 % – layer V. The thickness of layers enriched by organic matter is about 22,5 м (layer II), 11,0 м (layer III) и 13,5 м (layer IV). For them, the values of the hydrogen index vary from 670 to 700 mg HC / g TOC (layer II), from 530 to 600 mg HC / g TOC (layers III), from 500 to 700 mg HC / g TOC (layer IV), and the values of the oxygen index are from 30 to 40 mg CO₂ / g TOC, which indicates their high current oil and gas generation potential and the reducing conditions of the organic matter accumulation in the geological past.

The similar potential of rocks for sufficiently ancient Devonian sediments is explained by the fact that the Dmitrievskoye deposit is located on the northeastern outskirts of the Kuznetsk depression, and therefore it experienced a relatively smaller downwarping of the territory in comparison with the central parts of the depression.

As a result, sediment downwarping occurred in environments with relatively lower temperature and pressure. Given such potential of rocks and a temperature T_{max} exceeding 430 °C, we can conclude that the organic matter has reached the necessary maturity and entered the initial stage of the oil generation process.

The mineral carbon content for layers II, III, IV is not more than 6 %, which is typical for marly rocks. Moreover, MINC values exceeding 6 % already indicate the presence of carbonate rocks (layers I and V).

It should be noted that sampling was realized discretely and with an uneven increment since it was carried out from pits located at different distances from each other. In addition, each sampling point is characterized by a small number of samples.

Therefore, the boundaries of the distinguished layers and the obtained limits of changes of geochemical parameters need further refinement. However, for preliminary characterization of the organic matter in the rocks of the Dmitrievskoe deposit, this is quite enough.

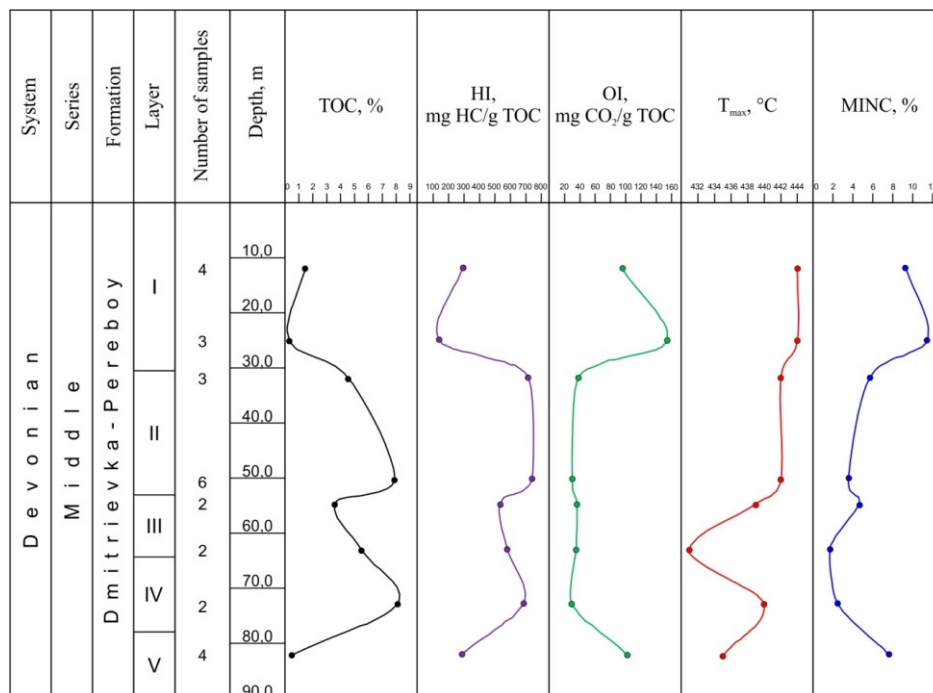


Fig. The geological and geochemical section of the Dmitrievskoe deposit

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QUANTUM-CHEMICAL CALCULATIONS OF THE THERMODYNAMIC PROPERTIES OF N-PARAFFINS HYDROCRACKING REACTIONS

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Every year the share of heavy and high-sulfur oils in the total volume of oil produced increases. Due to the peculiarities of climatic conditions and geographical location, the production of winter and Arctic brands of diesel fuel with corresponding low-temperature and environmental characteristics is of particular importance for Russia [2].

Long-chain paraffins of normal structure (C_{12} - C_{27}) have a significant influence on the low-temperature properties of diesel fuel. The main characteristics of the low-temperature properties of paraffins are: the cold filter plugging point, the freezing point and cloud point. The solidification temperature of long-chain n-paraffins varies from -10 °C for n-dodecane ($n-C_{12}H_{26}$) to $+60$ °C for n-heptacosan ($n-C_{27}H_{56}$).

In oil refining, the solution of problems to increase the yield, composition and quality of the obtained products, depending on the composition of raw materials and technological conditions of the process, is carried out using mathematical models that are developed on the basis of the physical and chemical regularities of the studied processes [5].

Currently, in order to conduct research on hydroprocesses, models based on grouping of components by fractions have been developed [4], as well as more detailed models based on combining reactants by groups: paraffins, naphthenes, and aromatic hydrocarbons [3]. However, these models do not take into account the distribution of n-paraffins and their reactivity in the target hydrocracking reaction.

To predict the low-temperature properties of the obtained diesel fuels, it is necessary to determine the number of long-chain n-paraffins in their composition. It is also established that n-paraffins in hydrocracking reactions have different reactivity [1]. In addition, during the hydrocracking reaction of n-paraffins, there is a different probability of breaking the bond in a particular position in the molecule, which also affects the yield and the ratio of the obtained products (gas, naphtha and diesel fraction, unconverted residue).